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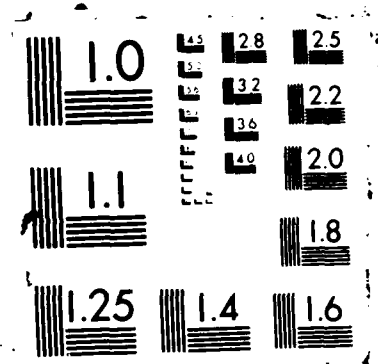
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MODIFICATION OF POLYSILANES

by

K. Matyjaszewski, Y. L. Chen and F. Yenca

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<p>New polysilanes bearing different alkoxy groups attached directly to silicon atoms were prepared by the displacement of the phenyl groups in the poly(phenylmethylsilylene) by trifluoromethanesulfonic acid and the subsequent reaction with alcohols in the presence of different bases:</p> $\begin{array}{ccccc} \text{Ph} & \text{HOSO}_2\text{CF}_3 & \text{OSO}_2\text{CF}_3 & \text{CH}_3\text{OH} & \text{OCH}_3 \\ & & & & \\ \dots\langle\text{Si}\rangle_n\dots & \longrightarrow & \dots\langle\text{Si}\rangle_n & \longrightarrow & \dots\langle\text{Si}\rangle_n\dots \\ & & & & \\ \text{CH}_3 & & \text{CH}_3 & & \text{CH}_3 \end{array}$ <p>This reaction was also studied for model compounds. Thus, different disilanes were converted to the 1,2-bis(trifluoromethanesulfonyloxy) tetramethyldisilane and subsequently to the corresponding 1,2-dialkoxydisilanes.</p>			
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MODIFICATION OF POLYSILANES

F. Yenca, Y. L. Chen and K. Matyjaszewski
Department of Chemistry
Carnegie-Mellon University
4400 Fifth Avenue
Pittsburgh, PA 15213

INTRODUCTION

High molecular weight polymers containing Si-Si bonds in the main chain are known for more than 30 years but due to the insolubility of the initially prepared polysilanes they were not studied in detail until recently. The successful conversion of poly(dimethylsilylene) to silicon carbide fibers and the subsequent preparation of soluble polysilanes gave rise to new studies of these materials¹. Polysilanes may find application in microlithography as imageable etch barriers², mid - UV solvent developed photoresists³, self-developing deep UV photoresists⁴, or contrast enhancement layers⁵. They were successfully used as catalysts for polymerization of vinyl monomers⁶. Polysilanes, after doping with strong electrophiles, showed strong increase of conductivity (10 orders of magnitude) to the level of semiconductors⁷. Polysilanes were also used to reinforce ceramics⁸ and, as mentioned before, they found application as precursors to silicon carbide fibers⁹.

The synthesis of polysilanes is based on the coupling reaction (Wurtz type) between alkali metals (Na, K, Li) and different dichlorodisubstituted silanes. In addition to the mixture of the relatively high molecular weight polymers ($M_n > 100,000$), low molecular weight polymer ($M_n < 5,000$), and some cyclic oligomers are formed¹⁰⁻¹². The yield of the high polymer is usually low. Some improvement was recently reported by varying the solvent and by inverse addition procedure.

In exploring new synthetic routes to linear well-defined polysilanes we used low temperature coupling reaction with ultrasonic activation of the sodium surface¹³. We have also been studying the ring-opening polymerization of the strained cyclic polysilanes¹⁴. The second route allows some variation in the structure of substituents at the silicon atom but the severe reaction conditions of a classical reductive coupling process limit the substituents structure to alkyl and aryl groups.

Polysilanes with functional side groups have not yet been prepared although they might have very interesting properties. For example, solubility of polymers could be varied in a controlled way, the physical, spectral, chemical, and conductive properties of polysilanes could also be influenced. Some substituents may increase stability of intermediate silylenes and facilitate photodegradation, some others may increase photostability of polymers.

We report below on some modifications of polysilanes and the relative studies with model compounds.

EXPERIMENTAL

¹H NMR spectra were recorded on either IBM model NR/80 spectrometer (at 80 MHz) or GE model 300 spectrometer (at 300 MHz). All chemical shifts are reported as parts-per-million (δ scale) from tetramethylsilane (TMS) using either TMS, methylene chloride or nitromethane as internal standards.

All experiments were carried out under dry nitrogen or argon atmosphere. Organic solvents and silicon halides were dried and distilled from calcium hydride prior to use. Preparation of 1,2-bis(trifluoromethanesulfonyloxy) tetramethyldisilane, (1) was described in detail in Ref. 16. The high molecular weight monomodal poly(phenylmethylsilylene) was prepared by reductive coupling reaction using ultrasonic bath¹⁵.

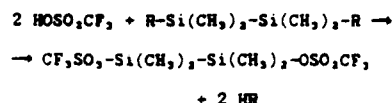
RESULTS AND DISCUSSION

Model studies.

We have used two disilanes as models of polysilanes: hexamethyldisilane and 1,2-diphenyltetramethyldisilane. These disilanes are known to be converted to the corresponding chlorides. However, reactivities of chlorosilanes are quite often insufficient for the complete modification of the polymer backbone, which requires rapid

reaction at concentrations lower than 10⁻³ mol/L. Therefore, we have chosen conversion to silyl trifluoromethanesulfonates, groups a few orders of magnitude more reactive than silyl chlorides in nucleophilic substitution.

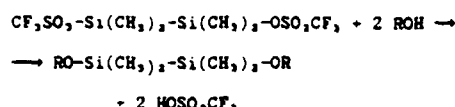
We have recently reported on the different methods of preparation of 1,2-bis(trifluoromethanesulfonyloxy)-tetramethyldisilane (1)¹⁶. This compound can be prepared in high yield from hexamethyldisilane, 1,2-diphenyltetramethyldisilane, or 1,2-dichlorotetramethyldisilane and triflic acid:



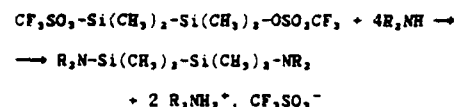
where R = Cl, CH₃, C₆H₅.

Ditriflate is stable at room temperature in the absence of moisture and can be easily distilled (bp = 87°C/5 mm Hg).

1,2-Dialkoxytetramethyldisilanes were prepared in the reaction of 1 with different alcohols:



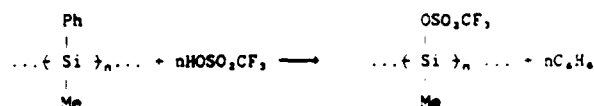
1 reacts also with amines. It forms disilylamines with secondary amines:



and pyridinium salts with pyridine.

Reactions on polymers.

Our model studies have shown that phenyl groups are cleaved much faster and much more efficiently than alkyl groups. Therefore, we have chosen poly(phenylmethylsilylene) as the starting material. Conversion of this polymer to the triflate derivative was followed by ¹H NMR. The broad signal of the phenyl groups in the initial polymer at the aromatic region was being replaced by the sharp singlet of benzene formed in this reaction:



Methyl groups even after replacement of the phenyl groups by triflate show a broad signal due to the tacticity of the polymer chain (Fig. 1a and 1b).

Displacement proceeds rapidly for the first 80% of the phenyl groups. No acidic protons at 9.3 ppm can be observed up to this conversion. Later displacement becomes more difficult, and small amount of the phenyl groups (less than 10%) remain even with the excess acid. This can be ascribed to the isotactic triads or pentads where bimolecular reaction of the acid can be hindered by the neighboring triflate groups.

Nearly completely substituted polymer is stable in chlorinated solvents (CH₂Cl₂, CHCl₃) and in aromatic solvents (C₆H₆, C₆H₅CH₃) in the absence of moisture. It reacts rapidly with moisture forming insoluble crosslinked polymer with siloxane linkages between chains. This reaction proceeds via formation of the silanol intermediates which rapidly condense with silyl triflates from the same or from different chains.

Modification of triflate substituted polysilane was carried out in the presence of amines using different alcohols as nucleophiles.

Reaction of triflate substituted polymer with pyridine led to the rapid precipitation of the polysalt. Later upon

addition of the methanol or butanol this precipitate was slowly being dissolved. NMR of the reaction mixture showed the presence of the protonated pyridine and poly(methylmethoxysilylene). Apparently the effect of the lacticity on the more remote alkoxy group is much smaller since a broad singlet of the methoxy group was found in the ^1H NMR spectra (cf. Fig. 1c). Similar effect was observed for vinyl ethers.

Reaction carried out in the presence of pyridine yielded some insoluble polymer probably due to the electrophilic attack of a polymeric silyl triflate on the p-C atom in the pyridine. Better results were obtained using triethylamine as a base trapping triflic acid. Molecular weight of polysilanes after modification decreases indicating some degradation of polymer.

Polysilane bearing several triflate groups in the backbone was used as initiators for the cationic polymerization of THF. This led to the graft copolymer with very high density of grafting. Molecular weight of this copolymer was equal to $M_n = 6.10^5$ and GPC analysis using RI and UV detectors showed no homopolymer of THF in this system.

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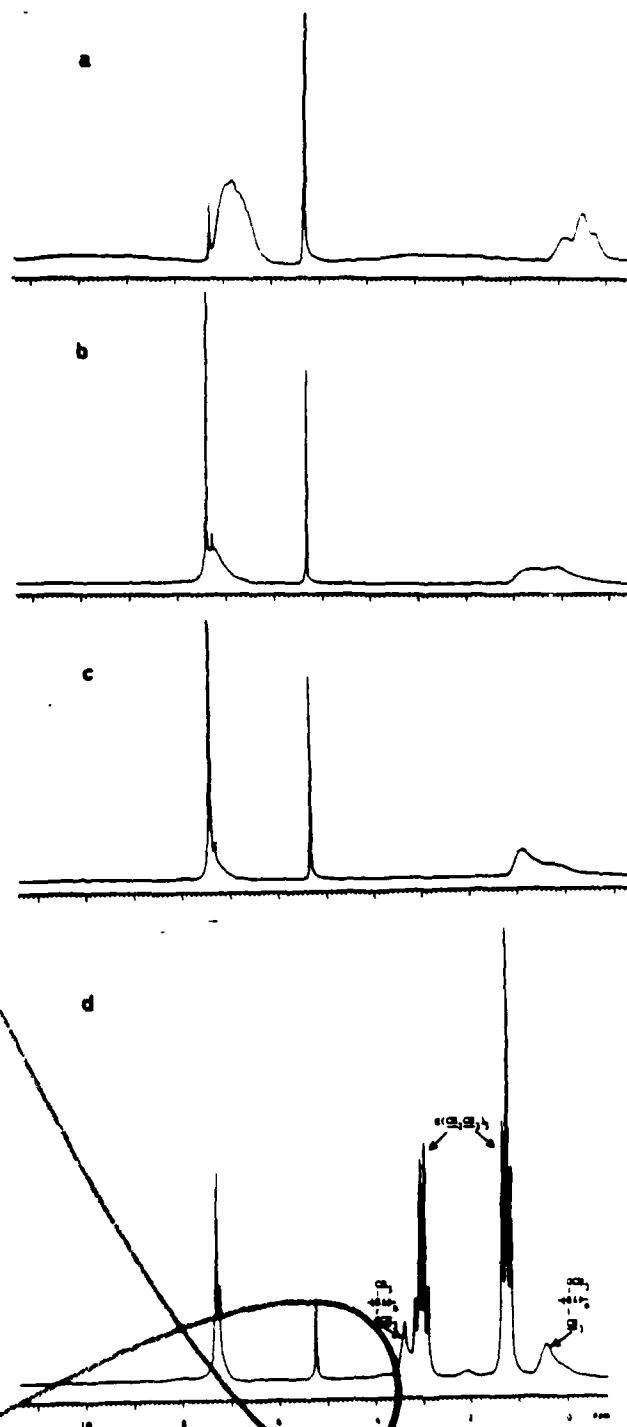


Fig. 1 ^1H -NMR spectra of poly(methylmethoxysilylene) ($[\text{SiPhMe}]_0 = 0.42\text{M}$) (a), after reaction with triflic acid ($[\text{HOSO}_2\text{CF}_3]_0 = 0.17\text{M}$) (b), ($[\text{HOSO}_2\text{CF}_3]_0 = 0.34\text{M}$) (c), and poly(methyl methoxy silylene) ($[\text{SiOMeMe}]_0 = 0.42\text{M}$) in CDCl_3 , solvent peak using CH_2Cl_2 as internal standard.

Modification of triflate substituted polysilane was carried out in the presence of amines using different alcohols as nucleophiles.

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Polysilane bearing several triflate groups in the backbone was used as initiators for the cationic polymerization of THF. This led to the graft copolymer with very high density of grafting. Molecular weight of this copolymer was equal to $M_n = 6.10^4$ and GPC analysis using RI and UV detectors showed no homopolymer of THF in this system.

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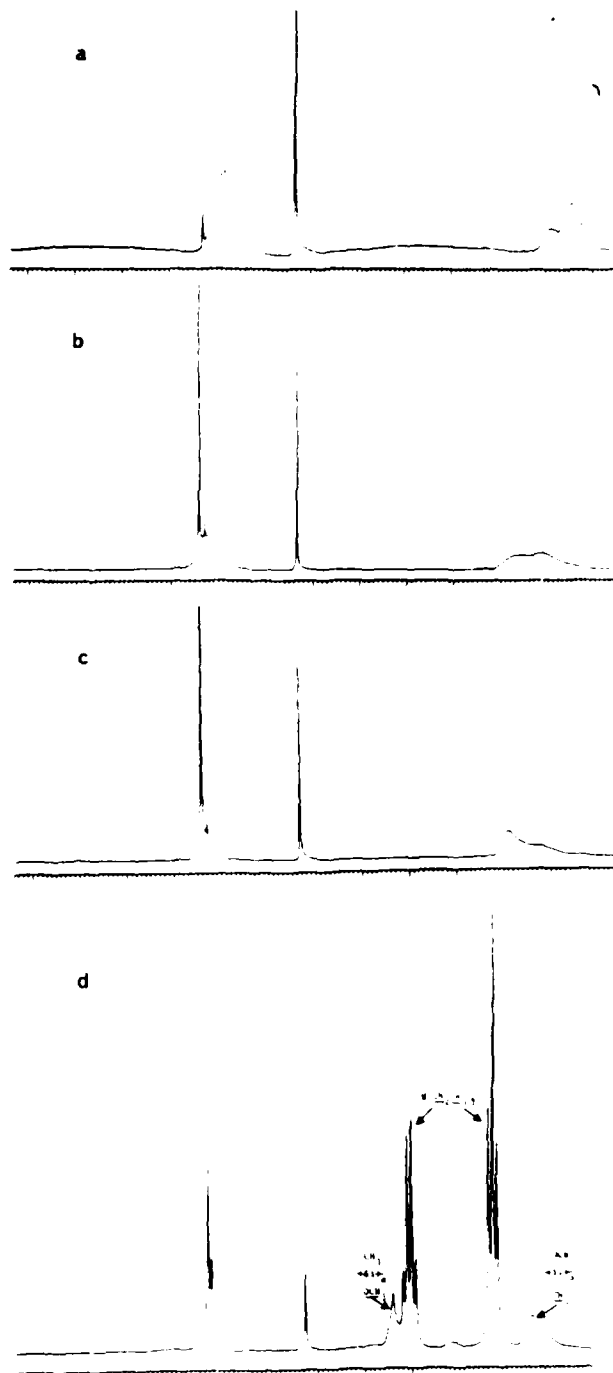


Fig. 1 ^1H NMR spectra of poly phenylmethyldisilylene $[\text{-SiPhMe}_2\text{-}]_n$ (0.42M) a, after reaction with triflic acid $[\text{HOSO}_2\text{CF}_3]_n$ (0.17M) b, $[\text{HOSO}_2\text{CF}_3]_n$ (0.34M) c, and poly methyl methyldisilylene $[\text{-SiOMeMe}_2\text{-}]_n$ (0.42M) in CDCl_3 solution using CH_2Cl_2 as internal standard.



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